I. Orthocyanbenzenesulphonic Acid.

II. The Action of Alcohols upon the High-melting Chloride of Ortho-sulphobenzoic Acid.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

WILLIAM JAY KARSLAKE.

1895.

EASTON, PA.:
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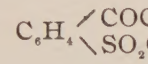
Part I.

ORTHOCYANBENZENESULPHONIC ACID.

Introduction.

Ever since the preparation of the chloride of orthosulphobenzoic acid by Remsen and Dolme[1] in 1889, there has been some doubt as to whether it was an individual substance, to be represented by one of the following formulae



I.

II.

or a mixture of both, as is now generally believed to be the case with phthalyl chloride. They, however, obtained no evidence pointing to its being a mixture and ascribed to it the symmetrical formula (I) upon the ground that chloro-ethers could be obtained by treating it with alcohols under certain conditions.

Two years later Remsen and Coates,[2] in studying the action of aniline upon the chloride, obtained two isomeric and well characterized anilides, the formation of which could not be very easily explained unless the chloride was regarded as a mixture made up of the two isomeric chlorides mentioned.

In the following year Remsen and Kohler[3] studied the behavior of the chloride towards various solvents and showed that it did not act as a single individual. They succeeded in obtaining a partial separation into crystals, which melted at 76°, and an uncrystallizable oil. They also found that of the two anilides described by Remsen and Coates only the one melting at 196° was formed when the solid chloride was used in the reaction, whereas the liquid chloride yielded both anilides, but the one melting with decomposition between 265°–280° in increasing proportion. Moreover, they showed it to be extremely probable that the solid chloride possesses the symmetrical formula. This they did as follows:

[1] Am. Chem. J., **11**, 332: Inaug. Diss., Johns Hopkins University, 1889.
[2] Am. Chem. J., **17**, 311.
[3] Am. Chem. J., **17**, 330.

Orthotoluenesulphone chloride was treated with aniline and gave orthotoluenesulphonanilide, which undoubtedly has the structure

$$C_6H_4\begin{cases}CH_3\\SO_2NHC_6H_5\end{cases}.$$

Upon oxidation this forms orthosulphanilidobenzoic acid,

$$C_6H_4\begin{cases}COOH\\SO_2NHC_6H_5\end{cases},$$

and this when heated, or treated with phosphorus pentachloride, gives

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}N.C_6H_5,$$

which is identical with the anil obtained by the action of aniline upon the solid chloride. These reactions leave little doubt that the solid chloride is to be represented by the formula

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}.$$

Still later, Remsen and Saunders,[1] in a further study of the behavior of the chloride towards solvents, succeeded in obtaining both chlorides in the crystalline condition, one melting at 76°–77°, the other at 21.5°–22.5°. Both chlorides gave orthosulphobenzoic acid when acted upon by water, but when treated with ammonia, their products were different. It was found that the high-melting chloride, which undoubtedly possesses the symmetrical formula, gave only the ammonium salt of saccharin and ammonium chloride, thus,

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}+4NH_3=C_6H_4\begin{cases}CO\\SO_2\end{cases}N.NH_4+2NH_4Cl,$$

while the low-melting chloride, on the other hand, gave as the principal product a salt which, in all probability, as Mr. Chambers[2] of this laboratory has shown, is the ammonium salt of orthocyanbenzenesulphonic acid. Bucher[3] had previously found that if the mixed chlorides were shaken for a few minutes in chloroform solution with aqueous ammonia,

[1] Am. Chem. J., **17**, 347.
[2] Am. Chem. J., **17**, 351. [3] Am. Chem. J., **17**, 349.

pure high-melting chloride was obtained, while the low-melting chloride was converted into a substance soluble in water. It was in studying this reaction that Chambers, upon evaporating the water-solution, obtained white botryoidal masses composed of minute needles which, at first, were thought to be the diamide

$$C_6H_4\begin{cases}C(NH_2)_2\\SO_2\end{cases}O,$$

corresponding to the unsymmetrical chloride

$$C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O$$

from which they were supposed to be obtained. Further study, however, showed, that in all probability, it was the isomeric ammonium salt of orthocyanbenzenesulphonic acid

$$C_6H_4\begin{cases}CN\\SO_2ONH_4\end{cases}$$

analagous to the ammonium salt of orthocyanbenzoic acid

$$C_6H_4\begin{cases}CN\\COONH_4\end{cases}$$

which Hoogewerff and Van Dorp[1] had obtained by treating phthalyl chloride in a corresponding manner with aqueous ammonia.

Presuming that the low-melting chloride has the unsymmetrical formula, its formation may be represented by the following equation:

$$C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O+4NH_3=C_6H_4\begin{cases}CN\\SO_2ONH_4\end{cases}+2NH_4Cl.$$

As further study, however, seemed desirable in order to place the formation of this salt and its composition beyond doubt, the work described in the following pages was taken up.

Preparation of Mixed Chlorides.

The method used at first for the preparation of the mixed chlorides was essentially that given by Saunders.[2] The acid

[1] Rec. Trav. Chim., **11**, 84; **12**, 12; **13**, 13.
[2] *Loc. cit.*; Inaug. Diss. Johns Hopkins Univ., 1894.

potassium salt of orthosulphobenzoic acid, which in turn had been made from commercial saccharin by the well-known method, was treated with two molecules of phosphorus pentachloride and the resulting oily-mass washed as well as possible with cold water. It was then solidified by surrounding it with a freezing-mixture and further washed by repeated trituration with ice-cold water in a mortar.[1] The chlorides so obtained were then carefully dried on a porous plate and kept in a desiccator over calcium chloride.

In spite of the great care taken in preparing the mixed chlorides by this method, a yield of only 70-80 per cent. could be obtained, the remainder being recovered from the wash-water in the form of the acid potassium salt upon evaporating to crystallization. This suggested that either the water used in washing decomposed the chlorides to some extent or that some orthosulphobenzoic anhydride was formed in the action of the phosphorus pentachloride upon the acid potassium salt. After several experiments the latter was found to be the principal cause and, in using the following method, almost theoretical yields were obtained. The dry acid potassium salt was thoroughly mixed in a porcelain evaporating dish with two and one-half[2] molecules of phosphorus pentachloride. After the reaction had ceased, the oily mass was poured into a flask and the phosphorus oxychloride distilled off under reduced pressure. The residual chlorides were then washed and dried as above mentioned. If the chlorides are to be immediately used for the preparation of the ammonium salt of orthocyanbenzenesulphonic acid, or for the high-melting chloride, by treatment with aqueous ammonia, the drying may be entirely omitted.

Preparation of Ammonium Orthocyanbenzenesulphonate.

A large number of experiments were made in the preparation of this salt in order to find those conditions which would give anything like a satisfactory yield. At first it was prepared by suspending the mixed chlorides in water and shaking them

[1] This method of final washing was devised by Mr. McKee, of this laboratory.
[2] These proportions were those found by Mr. McKee to be the best.

with dilute ammonia until a slight ammoniacal odor remained at the end of two or three minutes' shaking. The filtered solution was then evaporated upon the water-bath to crystallization when small botryoidal masses, composed of minute needles, separated, together with some ammonium chloride and ammonium salt of saccharin. These were filtered off with the aid of a suction-pump and carefully recrystallized from water. As thus obtained they are still very impure from contamination with ammonium chloride (?). The yield is from five to ten per cent. The next method used was similar to that which Bucher used in the preparation of the high-melting chloride except that dilute ammonia was taken instead of concentrated. The mixed chlorides were dissolved in chloroform and shaken with dilute aqueous ammonia until a slight excess remained after two or three minutes shaking. The water part of the solution was then evaporated to crystallization and from the ten grams of mixed chlorides used in the experiment, one and one-half grams of impure ammonium orthocyanbenzenesulphonate were obtained. The same experiment was repeated, using ether as the solvent, and from ten grams of mixed chlorides one and six-tenths grams of salt were obtained. The next method tried was one suggested by some work which Mr. Gray of this laboratory had done upon the mixed chlorides of paranitroorthosulphobenzoic acid. He found by adding excess of silver nitrate to the dilute water solution obtained by shaking the chlorides with ammonia, filtering from the precipitate, and evaporating to crystallization, that a difficultly soluble silver salt of paranitroorthosulphobenzonitrile was obtained. This method, however, did not give satisfactory results when applied to this investigation, since an extremely soluble silver salt is obtained which does not crystallize well. It had been noted in the above experiments that a considerable rise in temperature took place during the action of the ammonia upon the chlorides. It was thought that this might influence the yield of orthocyanbenzenesulphonic acid and the following experiment shows this to be decidedly the case. Since it was the method adopted in all later preparations of ammonium orthocyanbenzenesulphonate it will be given in detail. 30 grams of mixed chlorides were dissolved in about 125 cc. of ether

and placed in a 500 cc. separating funnel. Finely crushed ice was added and the whole shaken in order to thoroughly cool the ether. About 100 cc. of ice-cold water was now added and then dilute ammonia (1 : 5) in small portions at a time, shaking thoroughly after each addition until a slight excess remained after about two minutes' shaking. In the meantime crushed ice was frequently added so that there was always some present. The water solution was now drawn off, washed once or twice with ether, filtered, and evaporated to crystallization upon the water-bath. 9 grams of impure ammonium orthocyanbenzenesulphonate were obtained, which is a yield of 30 per cent. Generally, however, the yield obtained by this same method in after experiments was from 20 to 25 per cent. A word must also be said in regard to the crystallization of solutions from which the ammonium orthocyanbenzenesulphonate is to be obtained. At first the ammoniacal water solution was evaporated upon the water-bath to small bulk, so that, upon cooling, large quantities of ammonium chloride and the ammonium salt of saccharin separated out with the ammonium orthocyanbenzenesulphonate. The mass thus obtained, after being drained by the aid of the suction-pump, was placed in a beaker and treated with small quantities of cold water which dissolved the ammonium chloride and the ammonium salt of saccharin much more rapidly than it did the compact nodules of the ammonium orthocyanbenzenesulphonate. At its best, however, this is a poor method of separation, although at times, even later, it was found advantageous to resort to it. The method of treating the well-drained and perfectly dry mass with absolute alcohol, filtering from the undissolved ammonium chloride, and evaporating to crystallization, was also tried but did not give satisfactory results. It was found that the best and most satisfactory method consisted in evaporating the solution to such a concentration that crystallization began only after the perfectly cold solution had stood for a few hours. It seems that some time is required for the ammonium orthocyanbenzenesulphonate to arrange itself in crystalline form, that it has a tendency to form supersaturated solutions. It was frequently noticed that if the solution was too concentrated the ammonium chloride and the ammonium salt of sac-

charin would separate first, while, if the same solution was not so concentrated the ammonium orthocyanbenzenesulphonate separated first. As thus obtained, however, in the above described methods, the salt is still very impure, being contaminated with a large quantity of some chlorine compound from which it is extremely difficult to separate. Although it was taken for granted that this impurity was ammonium chloride, and, indeed, in many cases there can be no doubt that ammonium chloride, was present, still a further study in regard to this point seems desirable in order to find out if *only* ammonium chloride is present. After a large number of experiments it was found that alternate recrystallizations from absolute alcohol and from water furnished the salt pure, although, even by this method, at least 5 or 6 crystallizations were required. Repeated recrystallizations from absolute alcohol alone also gives good results. As thus obtained it crystallizes from alcohol in beautiful transparent needles arranged in rosettes, while from water it separates in botryoidal masses composed of radiating transparent needles. It is insoluble in ether and chloroform, very soluble in water and hot alcohol, but much less so in cold alcohol, from which it crystallizes best. Upon comparing some of this salt with some Mr. Chambers had previously obtained, it was found identical in all respects. Of the crystals,

I. 0.2014 gram gave 0.2376 gram $BaSO_4$ = 16.11 per cent. S.

II. 0.1988 gram gave 25.80 cc. nitrogen at 24°C., and 762.9 mm. = 14.58 per cent. N.

III. 0.2125 gram gave 0.2490 gram $BaSO_4$ = 16.10 per cent. S.

	Calculated for $C_6H_4<^{CN}_{SO_2ONH_4}$		Found.		
			I.	II.	III.
$C_7H_8O_3$	140	70.00	....	....	....
S	32	16.00	16.11	....	16.10
N_2	28	14.00	....	14.58	....
	200	100.00			

Analyses I and II are those of Mr. Chambers. The nitrogen was determined by the absolute method and the sulphur by the Carius method.

In several experiments where solutions were evaporated to crystallization in order to obtain the ammonium orthocyanbenzenesulphonate, there separated large beautiful transparent plates, which became dull and opaque after standing some time in the air. They were first obtained from a solution of nearly pure salt which had been put in a desiccator over concentrated sulphuric acid for evaporation and crystallization in the cold.

They were again obtained from a solution of 0.8 gram pure salt, which had been dissolved in 20 cc. of water and boiled with a return condenser for 2.5 hours. Lastly, they were obtained, and then in large quantity, upon evaporating the first water solution in order to obtain the first deposit of the ammonium orthocyanbenzenesulphonate. The plates were mechanically separated and dissolved in water for recrystallization. There separated, not the plates, but ammonium orthocyanbenzenesulphonate in its well-known form. Of the few plates which were obtained in the first observation

I. 0.4657 gram gave 0.5600 gram $BaSO_4$ = 16.52 per cent. S.
II. 0.4060 gram gave 0.4735 gram $BaSO_4$ = 16.02 per cent. S.

They suffered no loss upon heating to 190° C. The sulphur determinations were made by the Liebig method. Repeated experiments under apparently the same and other conditions were made in order to obtain enough of the salt for a complete analysis, but they were not obtained again.

From these few observations, and from the analyses, it would seem, however, that they were another crystalline form of ammonium orthocyanbenzenesulphonate, but further study upon this point is required.

Sodium Salt, $C_6H_4{<}^{CN}_{SO_2ONa} + H_2O$. —This salt has already been described by Jesurun,[1] who made it by treating orthocyanbenzenesulphone chloride with sodium hydroxide. It is also made by treating one molecule of the ammonium salt with one molecule of sodium hydroxide and evaporating to crystallization upon the water-bath. It crystallizes from concentrated solutions in large transparent prismatic plates contain-

[1] Ber. d. chem. Ges., **26**, 2288.

ing one molecule of water of crystallization. Of the crystals,

I. 0.2097 gram gave 0.2227 gram $BaSO_4$ = 14.59 per cent. S.
II. 0.1134 gram gave 0.1193 gram $BaSO_4$ = 14.45 per cent. S.
III. 0.2228 gram gave 0.2372 gram $BaSO_4$ = 14.62 per cent. S.
IV. 0.1920 gram lost 0.0158 gram at 150° = 8.23 per cent. H_2O, and gave 0.0613 gram Na_2SO_4 = 10.34 per cent. Na.

	Calculated for $C_6H_4<^{CN}_{SO_2ONa}+H_2O$.		Found. I.	II.	III.	IV.
$C_7H_4NO_3$	150.0	67.27	....	....	....	....
S	32.0	14.35	14.59	14.45	14.62	....
Na	23.0	10.31	....	....	....	10.34
H_2O	18.0	8.07	....	....	....	8.23
	223.0	100.00	....	....	....	....

There was no further loss in weight upon heating to 195° C. Analysis I is that of Mr. Chambers of the salt which he made.

Potassium Salt, $C_6H_4<^{CN}_{SO_2OK}$.—This salt is made by treating the ammonium salt with the calculated quantity of potassium hydroxide. It is much less soluble than the corresponding sodium salt, and crystallizes from moderately dilute solutions in small transparent needles radiating from a common center —in habit not unlike the ammonium salt. It is very easily prepared. Of the crystals,

I. 0.2128 gram gave 0.0830 gram K_2SO_4 = 17.61 per cent. K.
II. 0.2295 gram gave 0.0903 gram K_2SO_4 = 17.66 per cent. K.
III. 0.2550 gram gave 0.2824 gram $BaSO_4$ = 15.22 per cent. S.

	Calculated for $C_6H_4<^{CN}_{SO_2OK}$		Found. I.	II.	III.
$C_7H_4NO_3$	150.0	....	....	....	....
S	32.0	15.16	....	....	15.22
K	39.1	17.67	17.61	17.66	....
	221.1	....	....	....	....

The salt lost nothing in weight upon heating to 190° C.

Barium Salt, $\left(C_6H_4<^{CN}_{SO_3}\right)_2Ba+2H_2O$.—Considerable difficulty was experienced in preparing this salt.

There seemed to be a strong tendency for the nitrile group

to undergo saponification, thus giving rise to mixtures. The analyses given below are of some crystals which were used in the attempt to prepare the free acid and which were obtained by treating the ammonium salt with only three-fourths of the calculated quantity of barium hydroxide and gently heating upon the water-bath until no more ammonia was given off. It was then filtered, evaporated to small bulk, and crystallized from dilute alcohol. It separated in little tufts composed of white silky needles. They were washed with alcohol to free them from any ammonium cyan-salt which might be present. Of the air-dried crystals,

I. 0.1065 gram gave 0.0459 gram $BaSO_4$ = 25.34 per cent. Ba.
II. 0.1882 gram gave 0.0812 gram $BaSO_4$ = 25.36 per cent. Ba.
III. 0.1006 gram lost 0.0070 gram at 135° C. = 6.96 per cent. H_2O, and gave 0.0438 gram $BaSO_4$ = 25.59 per cent. Ba.

	Calculated for $(C_6H_4{<}^{CN}_{SO_3})_2Ba + 2H_2O$		Found. I.	II.	III.
$C_{14}H_8N_2O_6$	300.0	....	....	....	....
Ba	137.0	25.51	25.34	25.36	25.59
$2H_2O$	36.0	6.71	....	....	6.96
	473.0				

As stated above, this salt was used in the attempt to prepare free orthocyanbenzenesulphonic acid. It was dissolved in water, and dilute sulphuric acid carefully added until no further precipitation of barium sulphate took place. It was then filtered, evaporated to small bulk upon the water-bath, and placed in a desiccator over sulphuric acid. A syrupy, transparent mass was obtained, which slowly solidified into very fine needles arranged in rosettes. These were then washed with ether containing a little alcohol, and, finally, with ether alone. They melted at 181°–182° uncorrected. Of the crystals,

0.1880 gram gave 0.2037 gram $BaSO_4$ = 14.91 per cent. S.

The formulas, $C_6H_4{<}^{CN}_{SO_2OH} + 2H_2O$,

$C_6H_4{<}^{CONH_2}_{SO_2OH} + H_2O$, and

$C_6H_4{<}^{COONH_4}_{SO_2OH}$,

all agree for 14.62 per cent. S. by theory. Upon comparison, however, of its melting-point and method of crystallization with the orthobenzaminesulphonic acid described by Fahlberg and Barge,[1] and by Jesurun,[2] there can be little doubt of the identity of the two substances. Therefore its formula is

$$C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}+H_2O.$$

Not enough of the salt was obtained for a water determination. Other attempts were made to isolate the free acid by other methods but without success. Jesurun also failed to isolate it.

Transformation of Orthocyanbenzenesulphonic Acid into Orthobenzaminesulphonic Acid.

This transformation is most easily effected by boiling with excess of dilute alkalis. Hence it is, that in the preparation of the above described cyan-salts, great care is necessary in using no more than the calculated quantity of base.

In most cases the reaction proceeds in a normal manner according to the following equation:

$$C_6H_4\begin{cases}CN\\SO_2OH\end{cases}+H_2O=C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases},$$

and there stops, no further hydrolysis taking place to produce the corresponding ammonium salt as here represented:

$$C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}+H_2O=C_6H_4\begin{cases}COONH_4\\SO_2OH\end{cases}.$$

There were a few salts obtained, however, to which no formulae could be assigned.

Ammonium Salt, $C_6H_4\begin{cases}CONH_2\\SO_2ONH_4\end{cases}$.—This salt has already been prepared by Fahlberg and Barge,[3] and described as crystallizing from alcohol in white needles which melt at 255°–256°. Jesurun[4] describes it later as crystallizing from water in granular crystals containing one molecule of water of crystallization. These descriptions do not agree with the salt I obtained by

[1] Ber. d. chem. Ges., **22**, 759. [2] *Loc. cit.*
[3] *Loc. cit.* [4] *Loc. cit.*

boiling 3 grams of ammonium orthocyanbenzenesulphonate with dilute hydrochloric acid for 8 hours with a return condenser. Upon evaporating to dryness upon the water-bath several times to drive off most of the hydrochloric acid, there were obtained, by crystallization from a water solution, thin, transparent needles which contained no water of crystallization and which melted at 219°–220° uncorrected. A sulphur determination was made by the Liebig method. Of the crystals, 0.1918 gram gave 0.2058 gram $BaSO_4 = 14.74$ per cent. S.

The formula $C_6H_4 \begin{cases} CONH_2 \\ SO_2ONH_4 \end{cases}$ requires 14.68 per cent S.

Potassium Salt, $C_6H_4 \begin{cases} CONH_2 \\ SO_2OK \end{cases} + H_2O$. — This salt was made by boiling, with a return condenser, 3 grams of the ammonium cyan-salt with excess (3.5 grams) of dilute potassium hydroxide for 5 hours.

From a moderately concentrated solution there separated transparent monoclinic (?) prisms, which were once recrystallized from water. Of these crystals,

I. 0.2409 gram lost 0.0169 gram below 135° = 7.01 per cent. H_2O.

II. 0.1727 gram lost 0.0119 gram below 135° = 6.88 per cent. H_2O, and gave 0.0588 gram $K_2SO_4 = 15.28$ per cent. K.

III. 0.1103 gram gave 0.0376 gram $K_2SO_4 = 15.32$ per cent.

	Calculated for $C_6H_4 \begin{cases} CONH_2 \\ SO_2OK \end{cases} + H_2O$.	Found. I.	II.	III.
K	15.21	....	15.28	15.32
H_2O	7.00	7.01	6.88	....

There was no further loss in weight upon heating to 200° C.

Sodium Salt, $C_6H_4 \begin{cases} CONH_2 \\ SO_2ONa \end{cases} + 2H_2O$.—This salt was made just as the corresponding potassium salt by using sodium hydroxide, and was found to crystallize in transparent prismatic plates from moderately concentrated solutions. Of the crystals,

I. 0.3653 gram lost 0.0509 gram below 150° = 13.95 per cent. H_2O, and gave 0.1002 gram $Na_2SO_4 = 8.89$ per cent. Na.

II. 0.1894 gram lost 0.0263 gram below 150° = 13.88 per

cent. H_2O, and gave 0.0533 gram Na_2SO_4=9.12 per cent. Na.

	Calculated for $C_6H_4<^{CONH_2}_{SO_2ONa} + 2H_2O$.	Found. I.	II.
Na	8.88	8.89	9.12
$2H_2O$	13.85	13.95	13.88

No further loss in weight occurred upon heating to 195° C.

Barium Salt, $\left(C_6H_4<^{CONH_2}_{SO_2O}\right)_2 Ba + 5H_2O$.—This salt was made by boiling the ammonium cyan-salt for five hours with a large excess of barium hydroxide. The excess of barium hydroxide was then precipitated with carbon dioxide and the filtered solution evaporated to small bulk. It was found that crystallization did not easily take place even from syrupy solutions while from dilute alcohol it separated in white arborescent needles arranged in rosettes. Of these crystals,

I. 0.2490 gram gave 0.0928 gram $BaSO_4$ = 21.90 per cent. Ba.

II. 0.3375 gram lost 0.0477 gram below 140° = 14.13 per cent. H_2O, and gave 0.1262 gram $BaSO_4$ = 21.98 per cent. Ba.

III. 0.2169 gram gave 0.0812 gram $BaSO_4$ = 22.01 per cent. Ba.

IV. 0.2596 gram lost 0.0386 gram below 150° = 14.44 per cent. H_2O.

	Calculated for $(C_6H_4<^{CONH_2}_{SO_2O})_2Ba + 5H_2O$	I.	II.	Found. III.	IV.
Ba	21.85	21.90	21.98	22.01	....
$5H_2O$	14.35	....	14.13	....	14.44

No further loss in weight took place upon heating to 195° C.

A Calcium Salt was made in the same manner as the corresponding barium salt, and was found to crystallize in transparent needles. An analysis gave 10.34 per cent. calcium and 19.08 per cent. water lost at 185° C. No formula was found to agree with these results.

A Basic Lead Salt was also made for which no formula could be deduced. It was made by heating the ammonium cyan-salt upon the water-bath with large excess of freshly precipitated lead hydroxide until no more ammonia was given off and then filtering. Upon cooling there separated crystals

composed of white needles arranged more or less in rosettes. The air-dried salt lost no weight upon heating to 190° and gave the following results :

I. 0.2379 gram gave 0.2068 gram $PbSO_4$ = 59.34 per cent. Pb.

II. 0.1658 gram gave 0.1440 gram $PbSO_4$ = 59.33 per cent. Pb.

III. 0.1860 gram gave 0.1614 gram $PbSO_4$ = 59.29 per cent. Pb.

IV. 0.2735 gram gave 0.1634 gram $PbSO_4$ = 6.31 per cent. S.

V. 0.2772 gram gave 0.1634 gram $PbSO_4$ = 6.22 per cent. S.

Analysis III was of a second preparation of the salt. The lead was determined by ignition of the salt with addition of sulphuric acid and the sulphur by the Carius method.

Transformation of Orthocyanbenzenesulphonic Acid into Orthosulphobenzoic Acid.

This was accomplished by heating 2 grams of the ammonium cyan-salt with 15 cc. of hydrochloric acid (2 : 1) in a sealed tube for six or seven hours at 190° C. Upon evaporating to crystallization the characteristic rhomboidal plates of the acid ammonium salt of orthosulphobenzoic acid separated. Of these crystals,

0.4529 gram gave 0.4827 gram $BaSO_4$ = 14.64 per cent. S.

The formula $C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}$ requires 14.61 per cent. sulphur.

To further identify this salt it was treated with slight excess of potassium hydroxide, then acidified with hydrochloric acid and allowed to crystallize. The well-known orthorhombic plates of the acid potassium salt of orthosulphobenzoic acid were obtained, of which,

0.2839 gram gave 0.1033 gram K_2SO_4 = 16.33 per cent. K.

The formula $C_6H_4\begin{cases}COOH\\SO_2OK\end{cases}$ requires 16.35 per cent. potassium.

Conclusion.

From this investigation it is clearly evident that there is little doubt that orthocyanbenzenesulphonic acid is formed as one of the products of the action of ammonia upon the mixed chlorides of orthosulphobenzoic acid. Moreover, its formation can hardly be explained upon any other hypothesis than that it is derived from a chloride possessing the unsymmetrical formula

$$C_6H_4 \begin{cases} CCl_2 \\ SO_2 \end{cases} O.$$

If this be so, it appears highly probable that by the action of ammonia an imide is first formed which, being unstable under the existing conditions, goes over by intra-molecular change into orthocyanbenzenesulphonic acid, thus,

$$C_6H_4 \begin{cases} CCl_2 \\ SO_2 \end{cases} O \longrightarrow C_6H_4 \begin{cases} C:NH \\ SO_2 \end{cases} O \longrightarrow C_6H_4 \begin{cases} C\vdots N \\ SO_2OH \end{cases}.$$

Part II.

THE ACTION OF ALCOHOLS UPON THE HIGH-MELTING CHLORIDE OF ORTHOSULPHOBENZOIC ACID.

Introduction.

As already mentioned in the introduction of Part I, Remsen and Dohme studied the action of alcohols upon the chloride of orthosulphobenzoic acid, which at that time was believed to be a single individual. Subsequent investigations, however, having shown it to be a mixture, it was very desirable that their work be supplemented by a study of the action of alcohols upon the high-melting chloride and upon the low-melting chloride of which this mixture had been shown to be composed. Since large quantities of the high-melting chloride were obtained as a by-product in the preparation of orthocyanbenzenesulphonic acid, the study of the action of alcohols upon this chloride was taken up conjointly with the investigation described in Part I.

Preparation of High-Melting Chloride.

The ether, or chloroform, solution obtained in the preparation of ammonium orthocyanbenzenesulphonate is dried with calcium chloride, filtered, and evaporated to crystallization. Beautiful transparent prismatic needles or blocks are obtained which, after one crystallization from ligroin (boiling point 105°–140°), melt at 77°–78° C. The yield is 25–30 per cent.

Acid Esters of Orthosulphobenzoic Acid and Some of their Salts.

Practically the same results were obtained upon treating this chloride with boiling alcohols as were obtained by Remsen and Dohme. Acid esters are formed according to the following equation:

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}+3ROH=C_6H_4\begin{cases}COOR\\SO_2OH\end{cases}+2HCl+R_2O.$$

The best results were obtained as follows: The chloride was boiled with excess of alcohol in a small flask connected with a return-condenser for several hours. The excess of alcohol was then distilled off, a new portion of alcohol added, and the whole boiled again for about the same length of time. This was repeated until a drop of the solution, when put on a watch-glass, would give no crystals upon evaporating, or until the solution in the flask was almost free from hydrochloric acid, as shown by testing a little with silver nitrate. The acid esters as thus obtained are dark-colored acid liquids which are extremely soluble in water. None of them, at least by this method, were obtained in the crystalline condition. All of them undergo partial saponification when treated with water. The presence of a little alcohol, however, hinders this very materially. Their salts were made, in most cases, by the action of carbonates upon them.

Acid Methyl Ester, $C_6H_4\begin{cases}COOCH_3\\SO_2OH.\end{cases}$—This was made according to the method mentioned. It does not apparently differ from that obtained by Remsen and Dohme.

As will be seen later, it was probably obtained impure in the solid condition by another method. The following salts were made:

Silver Salt, $C_6H_4 \begin{cases} COOCH_3 \\ SO_2OAg \end{cases}$.—This was made by treating the acid methyl ester with silver carbonate, adding a little methyl alcohol, and evaporating to crystallization upon the water-bath. It separates in large thick, transparent plates, which are very soluble in water. Although the solution showed some decomposition due to exposure to light, the salt was easily obtained. It agrees with the salt described by Remsen and Dohme. Of the crystals,

0.2814 gram gave 0.0946 gram silver = 33.61 per cent. Ag.

	Calculated for $C_6H_4 \begin{cases} COOCH_3 \\ SO_2OAg \end{cases}$.	Found.
Ag	33.41	33.61

Calcium Salt, $\left(C_6H_4 \begin{cases} COOCH_3 \\ SO_2O \end{cases}\right)_2 Ca + H_2O$. — This was made in the same manner as the corresponding silver salt, and was found to crystallize in small white needles arranged in rosettes. Of the crystals,

I. 0.1996 gram lost 0.0070 gram below 200° C. = 3.51 per cent. H_2O, and gave 0.0556 gram $CaSO_4$ = 8.20 per cent. Ca.

II. 0.2446 gram gave 0.0685 gram $CaSO_4$ = 8.23 per cent, Ca.

	Calculated for $\left(C_6H_4 \begin{cases} COOCH_3 \\ SO_2O \end{cases}\right)_2 Ca + H_2O$.	Found. I.	Found. II.
Ca	8.19	8.20	8.23
H_2O	3.69	3.51	....

Copper Salt, $\left(C_6H_4 \begin{cases} COOCH_3 \\ SO_2O \end{cases}\right)_2 Cu + 4H_2O$. — This crystallizes from concentrated solutions in light blue prismatic needles arranged concentrically in groups. The copper was determined electrolytically. Of the crystals,

I. 0.1898 gram lost 0.0247 gram below 100° = 12.49 per cent. H_2O, and gave 0.0218 gram copper = 11.48 per cent. Cu.

II. 0.1685 gram lost 0.0214 gram below 100° = 12.70 per cent. H_2O, and gave 0.0190 gram copper = 11.27 per cent. Cu.

	Calculated for $\left(C_6H_4 \begin{cases} COOCH_3 \\ SO_2O \end{cases}\right)_2 Cu + 4H_2O$.	Found. I.	Found. II.
Cu	11.26	11.48	11.27
$4H_2O$	12.72	12.49	12.70

Strontium Salt, $\left(C_6H_4\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Sr+8H_2O$.—This crystallizes in beautiful transparent plates from concentrated solutions. Of the crystals,

0.2810 gram gave 0.0774 gram $SrSO_4 = 13.13$ per cent. Sr.

	Calculated for $(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix})_2Sr+8H_2O$.	Found.
Sr	13.14	13.13

Nickel Salt, $\left(C_6H_4\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Ni+6H_2O$.—This crystallizes in transparent green plates from concentrated solutions. Of the crystals,

0.2282 gram gave 0.0223 gram nickel = 9.77 per cent. Ni.

	Calculated for $(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix})_2Ni+6H_2O$.	Found.
Ni	9.67	9.77

The nickel was determined electrolytically.

Manganese Salt, $\left(C_6H_4\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Mn+4H_2O$. — This crystallizes in very thin transparent plates from concentrated solutions. Of the crystals,

0.1614 gram gave 0.0218 gram $Mn_3O_4 = 9.73$ per cent. Mn.

	Calculated for $(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix})_2Mn+4H_2O$.	Found.
Mn	9.88	9.73

Magnesium Salt, $\left(C_6H_4\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Mg+6H_2O$. — This crystallizes in large transparent plates. Of the crystals,

0.3161 gram gave 0.0684 gram $MgSO_4 = 4.32$ per cent. Mg.

	Calculated for $(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix})_2Mg+6H_2O$	Found.
Mg	4.24	4.32

The barium salt, which crystallizes in white needles arranged in rosettes; the *zinc salt*, which crystallizes in thin transparent plates; the *cadmium salt*, which crystallizes in thin broad needles; and the *lead salt*, which crystallizes in thin plates, were all made but for lack of time were not analyzed.

Acid Ethyl Ester, $C_6H_4 \begin{cases} COOC_2H_5 \\ SO_2OH \end{cases}$.—This was made in precisely the same way as the acid methyl ester. Although not obtained in crystalline condition by this method, it was probably so obtained by another method. It does not differ apparently from that described by Remsen and Dohme. The following salts were made:

Barium Salt, $\left(C_6H_4 \begin{cases} COOC_2H_5 \\ SO_2O \end{cases}\right)_2 Ba$.—This was made by treating the acid ethyl ester with barium carbonate, adding a little ethyl alcohol, and evaporating to crystallization upon the water-bath. It crystallizes in groups of small needles arranged in rosettes as described by Remsen and Dohme. Of the desiccator-dried crystals, 0.1436 gram lost no weight upon heating to 200° C., and gave 0.0558 gram $BaSO_4 = 22.85$ per cent. Ba.

	Calculated for $\left(C_6H_4 < \begin{matrix} COOC_2H_5 \\ SO_2O \end{matrix}\right)_2 Ba$	Found.
Ba	23.02	22.85

Since Remsen and Dohme describe the salt as containing 4 molecules of water of crystallization, it evidently loses this water when dried in a desiccator.

The Potassium Salt, which crystallizes in rosettes; the *copper salt*, which crystallizes in fine silky light blue needles; and the *magnesium salt*, were made, but were not analyzed for lack of time.

Acid Normal Propyl Ester, $C_6H_4 \begin{cases} COOC_3H_7 \\ SO_2OH \end{cases}$.—This was prepared in the same manner as the other acid esters, and possesses the same general properties. The barium salt was made.

Barium Salt, $\left(C_6H_4 \begin{cases} COOC_3H_7 \\ SO_2O \end{cases}\right)_2 Ba + 2\frac{1}{2}H_2O$. — This salt crystallizes in needles arranged more or less in rosettes. The salt loses two molecules of water of crystallization when dried in a desiccator. Of the air-dried crystals,

0.1991 gram gave 0.0692 gram $BaSO_4 = 20.44$ per cent. Ba.

Of the desiccator-dried salt,

0.4032 gram lost 0.0065 gram below 100° C. = 1.36 per cent. H_2O, and gave 0.1472 gram $BaSO_4$ = 21.46 per cent. Ba.

	Calculated for $(C_6H_4<^{COOC_3H_7}_{SO_2O})_2Ba+2\frac{1}{2}H_2O$	Found.
Ba	20.51	20.44

	$(C_6H_4<^{COOC_3H_7}_{SO_2O})_2Ba+\frac{1}{2}H_2O$	Found.
Ba	21.67	21.46
$\frac{1}{2}H_2O$	1.42	1.36

Chloro-Esters of Orthosulphobenzoic Acid.

In preparing these it was found that by continual action of cold alcohol upon the chloride the reaction went further than that expressed by the following equation:

$$C_6H_4<^{COCl}_{SO_2Cl} + ROH = C_6H_4<^{COOR}_{SO_2Cl} + HCl.$$

Two portions of chloride were dissolved in cold absolute methyl alcohol and in cold absolute ethyl alcohol respectively. Upon allowing the solution to stand some time, and the alcohols to evaporate spontaneously, oils were obtained, mixed with some crystals of chloride which had been unacted upon. They were repeatedly redissolved in their respective alcohol and allowed to evaporate spontaneously until crystals of solid chloride ceased to appear. In this manner oils were obtained as described by Remsen and Dohme for the chloro-esters. After standing about two months, however, it was found that both of them had solidified to a semi-crystalline mass. They were washed as well as possible with absolute ether, dried in a desiccator over concentrated sulphuric acid, and analyzed for chlorine and sulphur by the method of Carius. Only traces of chlorine were found in each salt. Of the methyl salt,

0.2068 gram gave 0.2227 gram $BaSO_4$ = 14.79 per cent S.

Of the ethyl salt,

0.2338 gram gave 0.2293 gram $BaSO_4$ = 13.48 per cent. S.

The formula $C_6H_4<^{COOCH_3}_{SO_2OH}$ requires 14.81 per cent. sulphur,

and the formula $C_6H_4\begin{cases}COOC_2H_5\\SO_2OH\end{cases}$ 13.91 per cent. sulphur.

Both salts are very hygroscopic and easily soluble in water giving acid solutions. It is evident, from these facts, that the chlor-esters first formed had been further acted upon by the alcohols giving rise to acid esters according to the following equation:

$$C_6H_4\begin{cases}COOR\\SO_2Cl\end{cases} + 2ROH = C_6H_4\begin{cases}COOR\\SO_2OH\end{cases} + HCl + R_2O.$$

In conclusion, the author wishes to take this opportunity of expressing his sincere gratitude to Prof. Remsen, at whose suggestion and under whose constant supervision this work was carried on.

JOHNS HOPKINS UNIVERSITY, May, 1895.

Biographical Sketch.

The author of this dissertation was born in LeRoy, Genesse County, New York, April 5th, 1869. His early educatian was received in public and in private schools of that town. In 1887 he entered Lafayette College, at Easton, Pennsylvania, and received the degree of Bachelor of Science in 1891 and Master of Science in 1894. During 1891–'92, he was private assistant to Dr. Wolcott Gibbs, at Newport, R. I., and during 1892–'93, he was Assistant in Analytical Chemistry in Pennsylvania State College, State College, Centre County, Pa. In October, 1893, he entered Johns Hopkins University as a student in Chemistry, Mineralogy, and Mathematics. During 1894–'95, he also held the position of Demonstrator in Chemistry in the University of Maryland.